SUMMARY

Air pollution has become an issue of great interest not only affecting the natural equilibrium of the biosphere, but also human health itself. Scientific evidence indicates that indoor-air can be seriously polluted and that presently people spend approximately 90% of their time indoors. Thus, the health risks incurred by breathing indoor air can significantly exceed the general limits of risk. The indoor-air quality problem should be regarded as one in which various pollutants interact in a synergistic manner to generate a health disorder.

Radon is the major pollutant in indoor air in most European countries and, in the Netherlands, where radon concentrations are relatively low (29 Bq m^{-3}), radon is estimated to induce about 800 (200-1400) fatal lung cancers per year among the 16 million inhabitants. To estimate the general risk posed by indoor radon, a well established policy has to be developed that includes not only the dose calculation, but also the identification of the sources of radon entry and their relative importance, the understanding and modeling at a fundamental level of the mechanism of radon transport. The 1995 second national radon survey in the Netherlands indicates that, for Dutch houses, 70% of the indoor radon concentration (the national average is 22 Bq m^{-3}) is due to exhalation from **building materials**, the remaining equally originating from the crawl space (15%) and from the outside air (15%). Also, from the broad range of building materials, concrete is the most widely used in the Netherlands. At present it is part of the focus of the Dutch government to calculate the Radiation Performance Index (RPI) based on the building plans. Standardised calculations include dose contributions from both gamma radiation and radon from the building materials. The expected radon concentration due to the sources of the house in one of its rooms is calculated from the designed ventilation characteristics of the building and the exhalation rates of the building materials.

The aim of the present thesis is to improve the basic knowledge on radon production and transport in concrete and to find ways to reduce the radon release by changes in production techniques or by the use of effective coatings.

The transport of radon in concrete is modeled at meso-scale level as a diffusion-driven[1] process. The physics of radon diffusion in homogeneous porous materials is described via a multi-phase time-dependent radon-diffusion equation that also accounts for production and decay. This equation has been so far used to validate radon transport in unconsolidated porous media (sand). To validate this model for the case of concrete, detailed information is needed on the radiometric properties of concrete components, characteristic porosity and pore-size distribution of concrete, moisture distribution, radon emanation and diffusion coefficients.

As in other earthly-materials, the source of radon in concrete is radium present in various components: sand, gravel and cement. Our measurements indicate that cement (in particular, ggbs cement) has the highest radium concentration (C_{Ra}), about one order of magnitude higher than the other components. Also the radon-release rate of dry ggbs cement is the highest of all components. However, if the C_{Ra} of concrete may be obtained as the weighted sum of the C_{Ra} of the components, for the case of radon-release rates the weighted sum of the dry components is one order of magnitude smaller than the radon-release rates determined for concrete. This difference disappears if the contribution of cement-powder is replaced by that of the hydrated cement paste. For hydrated cement the radon-release rate is an order of magnitude higher than for dry. **This implies that, in making concrete, radon release is increased over one order of magnitude.** The radon-release rate is thus dependent on the structural properties of the porous material. For cement, for example, the dry powder is highly dense packed compared to the hydrated cement paste in which gel pores are formed. It was concluded that it is of importance for concrete to understand the process of formation of the microstructure and how this is associated to the hydration of cement and moisture transport.

Under the assumption that highly compacted concrete (like ggbs concrete) may be well approximated as a homogeneous and uniform porous medium, represented by the cement paste, numerical calculations (DuCOM) show that a volumetric porosity of approximately 10% is characteristic for concrete. This result is in good agreement with our measurements. The numerical calculations also show that in concrete (cement paste approximation) the total porosity is distributed as follows: 40% corresponds to gel

[1] As most building materials have low permeability, advection is usually assumed to contribute only marginally under steady pressure gradients.

porosity, 35% to capillary porosity and the remaining 25% to interlayer porosity. The characteristic pore-size for the gel pores is about 10^{-9} m while for the capillary pores the distribution is centered around the value of 10^{-7}-10^{-8} m. Conclusively the pore-space in ggbs-concrete may be best described as being formed from capillary pores segmented by gel pores, this distribution resulting in a very dense and tortuous microstructure.

Gel pores are a product of the hydration of cement and their total volume (as well as the volume-ratio of gel and capillary pores) is dependent on the initial water-cement ratio. Actually, in concrete, water plays a very important role not only at early ages (initial mixture and curing) but during its entire life-time. Changes in environmental relative humidity can be translated in terms of internal moisture contents and moisture distributions and will consequently influence various types of transport. Most transport parameters thus, are also moisture-dependent.

With one of the methods we developed, the moisture-dependence of the radon-diffusion coefficient in concrete was investigated. This dependence is similar as for the case of sand with the only difference that the values are two orders of magnitude smaller. This fact is a direct consequence of the dense and highly tortuous microstructure of concrete due to the presence of gel pores in which Knudsen diffusion takes place. Thus, the overall mechanism of radon-diffusion is equivalent to a ``parallel connection" of the Knudsen and molecular diffusivities.

Unusual in concrete compared to sand is the moisture dependence of the emanation process, also a consequence of the compact and differently structured pore-space. In sand, radon emanation is never zero, even at zero moisture content. Already with a small increase in the moisture content an optimal/saturated value of the emanation coefficient is reached and preserved over the entire range. The emanation process in sand is relatively well explained by the recoil range of radon in air (63μm) and water (0.1μm) compared to the diameters of the capillary pores. In concrete the emanation coefficient as function of moisture is increasing linearly. As most surface area is formed by the gel pores, and gel pores also have the smallest diameters, an initial filling with water of the gel pores would be responsible for the linear increase of the emanation coefficient of radon at low moisture contents. Next, the capillary pores will start being saturated with water. As the two pore size distributions overlap, a continuously and linearly increase of the emanation is obtained.

Combined, moisture-dependent radon diffusion and emanation coefficients explain -in very good agreement with the experimental data- changes in radon-release rates for changing moisture content[2]. The fact that a homogeneous moisture distribution is sufficient to model the measured data is once more proving that the hypothesis of uniformity for concrete holds. According to numerical simulations of radon-release rates, a moisture distribution with a non-zero surface moisture would seem to better represent reality. Moreover, the moisture profiles obtained from DuCOM simulations show that for concrete the deviation from homogeneity takes place only over a surface layer of approximately 0.04 m. For radon release and transport, this layer is much smaller than the diffusion length of radon and hence its deviation is not of importance.

The combined experimental and numerical results presented in this thesis show that although concrete is a complex and heterogeneous porous medium, under some circumstances (highly compacted concrete), a good description is obtained by approximating the radon properties of concrete by considering the cement paste only. Under this assumption, the radon release from concrete most likely can be modelled on basis of the multi-phase radon transport equation and the results represent an additional validation of the multi-phase radon transport equation and its implementation. Combining this radon transport model with a model for concrete structure (DuCOM) will lead to a very powerful modelling tool for the design of low-radon producing concrete. Improvements of the modelling should mainly focus on a better assessment of the input parameters especially more information is needed on the moisture dependence of the emanation coefficient and the moisture distribution in the concrete. Also adsorption of radon to the internal surface in concrete, neglected so far, should be investigated.

The implications on the RPI of the modeling presented in this thesis are also investigated. Our calculations show that radon release from concrete in a dwelling is maximal for values between 30% to 70% of the relative humidity. Calculated with the RPI scheme, radon release from concrete overestimates the real production with 10-25%. Both, the RPI as our model calculations of the contribution of building materials to the indoor radon concentration are at least 50% lower than the values estimated in the second

[2] The variation of radon-release rates with changing moisture content may be also regarded as the main mechanism responsible to the time-dependence of the radon-release rates.

Dutch radon survey. This indicates that there is still an unaccounted process that contributes significantly to the indoor radon concentration. Both RPI and our model is based on quantities which are determined for diffusion-only conditions which may not be the real case. As previously observed, small pressure differences may change the radon source strength of soil by an order of magnitude. If such mechanisms are also present for building materials such as concrete, the mismatch between calculations and data may be explained. Of course, it has to be seen if this unknown mechanism acts in the same way for all building materials.

The alternative method to reduce radon release is represented by surface covering. The reduction efficiency of various sealants and membranes when applied on concrete were experimentally investigated. Our conclusion is that usually coverings that can easily be applied on the surface of concrete do not exhibit good radon-reduction properties. So far the only candidate that almost totally reduces radon release from concrete are the high-performance reinforced polymeric membranes (PMMA and PPTA). To be able to design a radon-effective polymeric membrane, a theoretical study is needed. As a part of the present thesis, a method employing Molecular Modelling and Monte Carlo techniques was proposed that will prove useful for such research. It is also proposed to future investigate the possible use of polymer-clays nanocomposites as radon barriers.

The research described in this thesis intends to offer a more thorough understanding of transport of radon in concrete by using all the three types of methods available to science nowadays: experiments, theory and computer simulations. These tools, integrated into a fundamental approach, led to a more accurate picture of the physical phenomena and to conclusions that are of interest for various areas as: radon research, concrete industry, indoor air pollution control, environmental science.